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NRL REPORT C-3478

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THE SILVER OXIDE-ZINC ALKALINE PRIMARY CELL

PART 1

EFFECT OF TEMPERATURE AND OF VOLUME AND
CONCENTRATION OF ELECTROLYTE ON THE RELATIONSHIP B
CAPACITY AND CURRENT DENSITY FOR A CELL USING SHE
NEGATIVE PLATES

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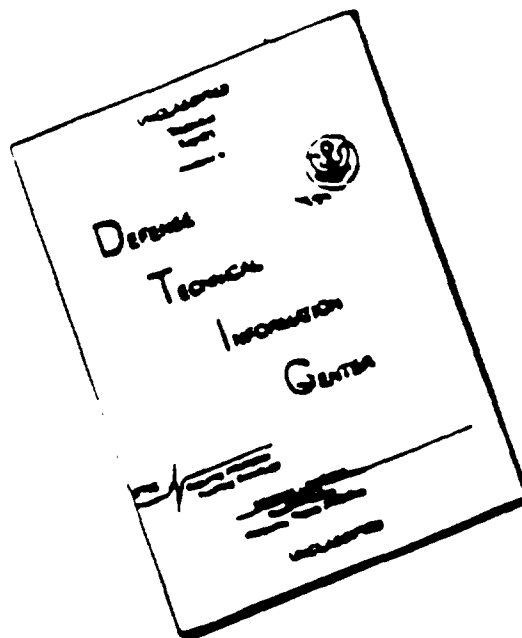
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Subj: "The Silver Oxide-Zinc Alkaline Primary Cell";
Amplification of.

1. Problem Status, p. iv, should read:

"This report is the first in a new series on this problem.
Previous reports on the problem are cited in the Refer-
ences, p. 27. Work is continuing."

2. Page 2, line 10, should read:

". . . of a new series presenting . . ."

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THE SILVER OXIDE-ZINC ALKALINE PRIMARY CELL

PART 1

EFFECT OF TEMPERATURE AND OF VOLUME AND
CONCENTRATION OF ELECTROLYTE ON THE RELATIONSHIP BETWEEN
CAPACITY AND CURRENT DENSITY FOR A CELL USING SHEET-ZINC
NEGATIVE PLATES

C. M. Shepherd

July 1, 1949

Approved by:

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ABSTRACT

The outstanding properties of the silver oxide-zinc alkaline cell are its low weight, high current capacity, constant voltage, and high capacity at low temperatures. It is a primary cell of low shelf life containing an alkaline (KOH) electrolyte which is added immediately before use. During cell discharge, silver peroxide is reduced to silver at the positive electrode, and zinc is oxidized at the negative electrode.

Experimental work, subjected to statistical control, showed that cell failure always occurs at the negative electrode if sufficient silver oxide is present at the positive plate. Presence of copper diminishes cell capacity. The physical structure of the silver electrode, and the method of preparation and of anodizing, can all be varied over wide limits without affecting cell capacity. Variations in electrode height and spacing do not affect cell capacity.

All experiments were made using high-purity, sheet-zinc negative electrodes. It was found that cell capacity is directly proportional to electrolyte volume, to electrolyte concentration, and to amount of KOH present in the electrolyte, within certain limits which cover almost all cell designs. The effect of current density and temperature on cell capacity can be expressed by the following equations:

$$\log K = 1.0412 - 1.5971 \log I - 0.2575(\log I)^2 \text{ at } 60^\circ\text{C.}$$

$$\log K = 1.0016 - 1.602 \log I - 0.210(\log I)^2 \text{ at } 40^\circ\text{C.}$$

$$\log K = 0.9242 - 1.707 \log I - 0.238(\log I)^2 \text{ at } 20^\circ\text{C.}$$

$$\log K = 0.4194 - 2.61 \log I - 0.615(\log I)^2 \text{ at } 0^\circ\text{C.}$$

$$\log K = -1.5325 - 4.959 \log I - 1.38(\log I)^2 \text{ at } -20^\circ\text{C.}$$

where K is cell capacity in minutes per gram of KOH per square inch of negative electrode area, and I is the current density in amperes per square inch.

PROBLEM STATUS

This is an interim report; work is continuing.

AUTHORIZATION

NRL Problem C05-06R

THE SILVER OXIDE-ZINC ALKALINE PRIMARY CELL

Part 1

Effect of Temperature and of Volume and Concentration
of Electrolyte on the Relationship Between Capacity and Current Density
for a Cell Using Sheet-Zinc Negative Plates

Because of its desirable characteristics, there is considerable demand, based largely on minimization of weight or volume for a given electrical output, for the silver oxide-zinc primary cell. It will deliver more power per unit weight of active material than any other known type of primary battery.^{1*} It is capable of operating satisfactorily at extremely high current densities,¹ as much as 1000 amperes per square foot of electrode area having been obtained during a short discharge. Another outstanding characteristic of the silver oxide-zinc alkaline cell is the constant voltage maintained under various operating conditions.^{1,2} Moderate changes in temperature, current density, and electrolyte concentration have only a slight effect on the emf of the cell, usually less than one-tenth of a volt variation occurring during the major portion of a complete discharge. In addition, the cell has shown an excellent possibility of fulfilling the demand for a low-temperature high-capacity primary battery.

The cell, however, has a high rate of self-discharge (a fact which makes it necessary to add the electrolyte immediately before use^{2,3}) because of the dissolution of the silver oxide in the electrolyte and consequent diffusion to the negative electrode where it reacts with the zinc.² This factor has been one of the chief drawbacks in the various attempts that have been made to use the system as a basis for a secondary battery.³ Although some work has been done in developing separators which will retard the migration of the silver oxide and thereby increase the shelf life,⁴ much still remains to be done in this direction.

Besides this objection, the manufacture of the silver cell presents certain problems peculiar to itself. For example, the majority of the demands for each cell are such that a specially designed cell will be required for each particular need. This is especially true wherever the demand is for a cell of minimum weight or volume. It is not possible to manufacture a few standard cell types which can be assembled in various ways to fulfill any particular requirement. The cell of minimum weight for a given current density will not be the cell of minimum weight for any other current density. In the manufacture of ordinary batteries, enough of each cell component is used to insure the fulfillment of a wide range of requirements. But in the case of the silver cell, the weights or volumes of the cell components are often minimized in relation to a particular set of operating conditions. Therefore, efficient cell design is not possible until the characteristics have been thoroughly evaluated.

Moreover, in some applications premature failure of the silver cell would have grave consequences. In such cases it is extremely important for the cell to be able to meet its specifications. Often this will present two diametrically opposed possibilities, namely,

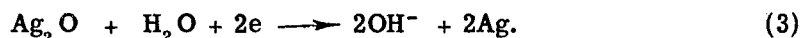
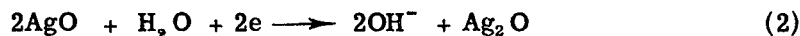
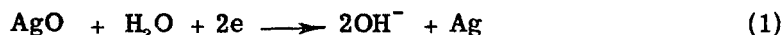
* See reference list at end of report.

increase of the amounts of the various cell components to insure the cell will have the required capacity, and decrease of the amounts of the various cell components to give minimization of cell weight or volume. These two factors may be balanced readily if statistical methods are used in cell production. The methods of quality control are particularly applicable in such cases.

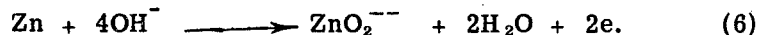
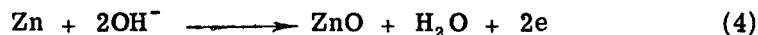
Because of a great potential usefulness for the silver cell, it is desirable to understand its characteristics in as complete detail as possible. Work done at the Bureau of Standards early in the war stimulated the interest of the Bureau of Ships, who subsequently requested the Naval Research Laboratory to make a thorough study of the cell. This report is the first of a series presenting results of NRL's participation in solution of the problem.

REVIEW OF THE CELL REACTIONS

The cell consists of a negative electrode of zinc, a positive electrode of silver peroxide, and an alkaline electrolyte which is generally KOH solution. The silver peroxide in the positive electrode is reduced during discharge to metallic silver, either in one step as shown in equation 1, or in two steps as shown in equations 2 and 3.



The negative electrode of metallic zinc is oxidized on discharge, and experimental evidence indicates that one of the three following reactions takes place:



The potentials of these reactions under certain conditions are comparatively close together and consequently cannot readily be used for their identification.

When the zinc concentration in the electrolyte becomes sufficiently high during a cell discharge a visible film is formed on the surface of the negative electrode. By means of X-ray diffraction after air-drying or after drying in nitrogen, this film has been identified as zinc oxide. There is, of course, some possibility that the film changes in composition during the time it is removed from the cell and allowed to dry. If the reaction proceeds in agreement with equations 4 or 5, any zinc oxide or hydroxide formed would immediately dissolve in the electrolyte until the solution was saturated, and then a visible film would form on the electrode. If, in agreement with equation 6, the zinc went into solution as a zincate, the highest concentration of this compound would be in the film of liquid on the electrode surface. At a sufficiently high concentration, this compound may decompose and precipitate a film of zinc oxide or hydroxide on the electrode.

In the first case, the potassium hydroxide does not enter directly into the cell reaction, and in the second case it is regenerated according to some equation such as:



It should therefore be possible to obtain, from a given amount of potassium hydroxide, a greater cell capacity than would be predicted from the equation:



which latter represents the least amount of potassium hydroxide that can enter into an electrode reaction. This possibility has been verified in low current density cell discharges which gave electrode efficiencies as high as 145 percent on the basis of equation 8.

Single electrode measurements made with a reference electrode, Hg-HgO-KOH, showed that failure at the end of a discharge always occurs at the negative plate.⁵ This failure may be attributed in part to the film of solids which deposits on the zinc electrode and retards the diffusion of the electrolyte and partially to concentration polarization in the liquid film adjoining the electrode surface.

EXPERIMENTAL METHODS

A test cell assembly must be constructed in a manner that leaves no doubt about the cause of cell failure at the end of a discharge. Since a number of new factors were to be studied, several variations were made in the test cell assembly previously adopted as a standard.⁵ Failure of the negative electrode was necessary in every discharge so that it would be possible to determine how the cell was affected by various factors. The excess of positive material, necessary to insure negative electrode failure, was obtained by using one negative and two positive electrodes, each 1 1/2 inches square. The total area for both sides of the negative electrode was approximately 4.26 square inches, after deduction of the area covered by the spacers. This electrode was prepared from 0.020-inch, high-purity sheet zinc. The spacers, which were 0.060-inch wide and 1.5-inches long, were cut to the desired thickness from polystyrene sheet. Two spacers were cemented vertically to each side of the negative electrode with polystyrene cement.

For the positive plate, a grid of 40 x 30-mesh screen of suitable material was pasted with a mixture prepared from 5 grams of silver chloride and a few drops of 25% potassium hydroxide, and then allowed to dry in air. Subsequently, the plates were oxidized anodically in a solution of 15% potassium hydroxide at 0.25 ampere for 24 hours, soaked in distilled water for one day, and then air-dried. Since these conditions were not critical, they could be varied over a wide range. When completely charged, the plate is entirely black with no brown spots of Ag₂O remaining. The total potassium hydroxide content of the plate, after washing and drying, was not more than a few milligrams.

Cell cases, stamped from sheet polystyrene, were of the same cross-section as previously used⁵ and could be made any desired thickness. The dimensions were 2 5/8 inches high and up to 9/16-inch thick. The electrolyte, normally 10 cc of potassium hydroxide at a given concentration, was added until its level was slightly above the top of the electrodes. The cell was discharged immediately after the addition of the electrolyte. All discharges were made at constant temperature and at a constant current, the voltage being recorded automatically.

The cell discharge was considered complete when the emf had dropped to 1.0 volt. Since the cell voltage is essentially constant throughout a discharge, the emf at the time the cell is two-thirds discharged has been found to be essentially equivalent to the average discharge voltage and was considered to be the representative voltage of the cell.

STATISTICAL CONTROL OF EXPERIMENTAL METHODS

In determining the basic principles of cell operation, the usual procedure would be to hold constant all but one variable and to determine the effect of that one. However, it is almost impossible to control each variable individually because so many factors may enter into the operation of a cell. Control is further complicated by the fact that the nature of an electrolytic solution is greatly affected whenever relatively small quantities of various substances are present. It therefore becomes necessary to study these factors to determine which may affect cell operation. Once these are known, it should be possible to duplicate results consistently. Actually, there will always be an appreciable variation which cannot be eliminated. Therefore, statistical methods can often be used to advantage, particularly when the variations are not small.

In the case of the silver oxide-zinc alkaline cell, the variations are fairly large, as may be noted in Figure 1 where the estimated standard deviation, σ , is plotted against cell capacity. The presence of uncontrolled factors and other statistical considerations have caused the data in Figure 1 to be somewhat irregular. However, the graph does show qualitatively the large increase in the standard deviation with increase in cell capacity.

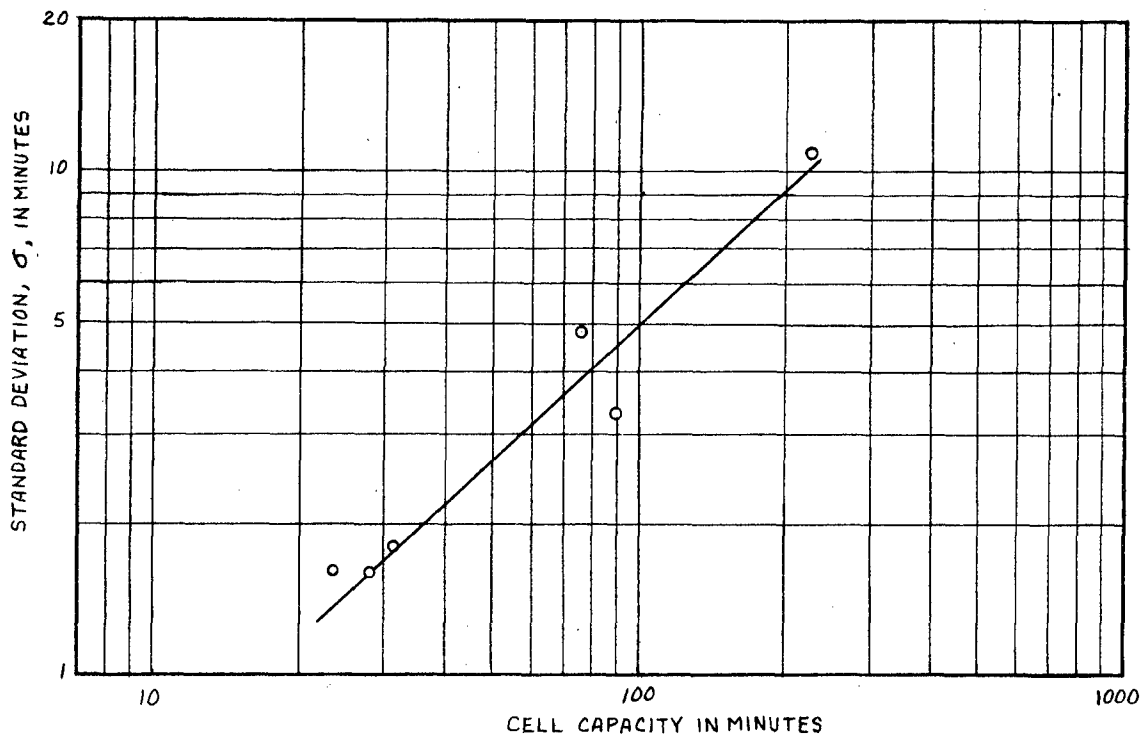


Figure 1 - Variation of standard deviation with cell capacity

The standard deviation, σ , can be considered to be a statistical measure of the variation obtained in repeating an experiment under the same conditions. If a large number of readings are taken, 95.4 percent of them will fall within $\pm 2\sigma$ of the mean, while 99.7 percent will fall within $\pm 3\sigma$ of the mean. If, out of 1000 measurements made of a particular cell capacity, the average reading was found to be 80 minutes and the standard deviation was 4 minutes, then approximately 954 of the readings would lie between 72 and 88 minutes.

and 997 of the readings would fall between 68 and 92 minutes. Approximately 999 times out of 1000, cell capacity would exceed 68 minutes when the cell was designed for an average life of 80 minutes. Utilization of the standard deviation in this manner suggests a simple method for calculating safety factors. However, in the design of a cell, laboratory results cannot be used for predicting safety factors in cell manufacture, since differences in construction and assembly can cause a large variation in the standard deviation.

A variation in results as large as those indicated in Figure 1 can cause other difficulties. In testing the effect of a particular factor, the question arises as to whether the variation obtained could have occurred by chance or whether it was actually caused by that factor. The t test of significance can often be used in such a case.⁶ A particular modification of the chi square (χ^2) test of significance, applicable to any problem where a new factor is being tested, has been developed for this problem.* The main use of statistics here was to design the experiment so that the conclusions might readily be reached, to prove mathematically conclusions that might otherwise be questionable, and to reduce materially the possibility of forming deductions from insufficient data.

From theoretical considerations, the factors which may affect the capacity and characteristics of a cell are temperature, current density, quantity and physical conditions of active materials in the positive and negative electrodes, quantity and composition of electrolyte, spacing of electrodes, and other physical dimensions of the cell, as well as its previous history. Some of these factors are almost impossible to define, and some may be very susceptible to change. It is not possible, nor is it desirable, to evaluate the effects of varying all of these factors. However, if the effect of varying any one of them is to be determined, it is necessary that all the rest of them be controlled. Control may be obtained by varying several factors at once in a particular manner, as in the method of factorial analysis, or by holding them all constant and varying the one to be evaluated. To obtain statistical control, it is necessary to employ one of the following methods:

- (a) Control the variation occurring in the factors by a particular method;
- (b) Keep constant the factors not being tested; or
- (c) Prove that the system is not affected by any variation in the factors not being tested.

The latter two methods were used in studying the silver oxide cell. It is not always necessary to know what the particular factors are in order to use these methods. However, it is necessary to assume, until proved otherwise, that any change made in the system may cause a variation in the results obtained.

During the construction of several hundred cells, many new factors were introduced which had to be brought under statistical control before the major factors affecting the cell characteristics could be evaluated. An example of this occurred in connection with the preparation of the negative electrode from a high-purity sheet zinc obtained from the New Jersey Zinc Company. Three lots from the same melt were tested, and one was found to give slightly lower cell capacities. Whether this was due to impurities or to metallurgical treatment is a problem for future investigation.

*This method will be described in a future NRL report.

DATA AND DISCUSSION OF RESULTS

Effects of Copper

When an attempt was made to duplicate the work of previous investigators, a variation in results was obtained which indicated the presence of an uncontrolled factor. Examination of the data showed that the variation occurred between cells using new positive electrodes and cells using recharged positive electrodes. The cause of this trouble was traced to contamination of the cell with copper. When copper salts are added to the electrolyte, the cell capacity is greatly reduced.

The procedure for preparing a positive electrode had been to silver-plate a grid of 40 x 40-mesh copper screen, paste with silver chloride, and anodize by the procedure previously described. New electrodes prepared in this manner generally give good results. Since the present status of the silver oxide cell is such that it can be used but once and then must be discarded, a properly silver-plated copper grid should prove satisfactory. However, there is a possibility of the electrolyte becoming contaminated with copper if the silver-plate is eaten through during anodization. The positive plates can be removed from a used cell and be recharged for further reuse. When this is done, the cell capacities are reduced and copper compounds can often be detected on the surface of the positive. Table 1 shows qualitatively the percentage reduction of the copper-free cell capacity obtained when a recharged positive electrode with copper grid is used. The term, cell capacity, as used in this report denotes the time in minutes that a particular discharge will last. The number of cycles which a particular electrode has experienced varies at random in Table 1. It is highly probable that the results obtained were considerably affected by the number of cycles and the severity of the cycling conditions.

TABLE 1
Reduction of Cell Capacity (%) Due to Copper Contamination
(Negative Electrode - Sheet Zinc)

Temperature	Current Density	20% KOH	30% KOH	40% KOH
0°C.	0.235 amps. per sq. in.	20	36	5
			37.5	
	0.470 amps. per sq. in.	75	45	75
		45	17	60
		73		8
	1.175 amps. per sq. in.		45	
20°C.	0.117 amps. per sq. in.			24
	0.235 amps. per sq. in.	8.5	3	5
				32.5
	0.470 amps. per sq. in.	53	42	21.5
			15	25
	1.175 amps. per sq. in.	17	38	0
			3	
40°C.	0.235 amps. per sq. in.	48*	30	11
	0.470 amps. per sq. in.	57*		
	1.175 amps. per sq. in.	29*		
		38*		

* Increase in capacity.

Obviously the presence of copper is very deleterious although the mechanism by which it affects cell operation is obscure. Measurements made with a half-cell showed that the negative electrode fails first, even though the positive electrode contains the copper which diminishes the cell capacity.

Positive Grid Material

These results show the desirability of making the grids in the silver cell from some material other than copper. Silver screen (40 x 33-mesh) was tried as a positive grid with excellent results. Plates were prepared in the usual manner using silver screen grids and were discharged in a cell. They were subsequently removed, soaked in distilled water for 24 hours, recharged, and used again. Positive plates prepared in this manner were duplicating original results after being used as many as twenty times. Over 100 positive plates were prepared in this manner without a single failure. Adherence is good, and the only sign of wear is mechanical.

In spite of its excellence, the high cost of silver and its high specific gravity (which latter makes for a heavy grid) make it desirable to find a more suitable positive grid material. A 40 x 40-mesh nickel screen was cleaned and used as a grid for positive plates. Cell capacity was almost equivalent to that obtained with silver grids even though the adherence of the active material was poor. This difficulty was believed to be due to the nickel oxide formed on anodization. It is possible that a silver-plated nickel screen would make a good positive grid.

The grid weight is an appreciable portion of the total cell weight. Since minimization of cell weight may often be a requirement in cell design, both aluminum and magnesium should be excellent grid materials. Preliminary tests made with uncoated magnesium were highly unsatisfactory due to the formation of a gelatinous magnesium compound. Aluminum reacts vigorously with the electrolyte at slightly elevated temperatures. These difficulties might be overcome, however, by covering the grid with an electroplated deposit of an inert metal. Until further developments are made, a properly silver-plated copper grid should prove satisfactory for use in the primary cell. If the positive plate is going to be recharged for further use, then a silver-screen grid should be used.

Preparation of the Positive Plate

Other methods of preparing the positive plate were studied in an attempt to improve its many undesirable characteristics such as rough surface, high porosity, presence of loose particles, tendency to shed, and susceptibility to physical disintegration. Several satisfactory substitutes were developed which eliminated most of these difficulties. The introduction of a new type of positive plate presents a new variable which may affect cell capacity. The probability of such an occurrence is small since the negative plate is the first to fail. However, it is advisable to check this experimentally, since it has already been shown that a variation (copper contamination) in the positive plate materially affects cell capacity.

Different methods of applying the silver chloride to the grid were tried. The regular method consisted of forming a stiff paste of five grams of silver chloride and a few drops of potassium hydroxide solution. This was pasted onto the grid by means of a spatula and air dried. Plates of lower porosity were formed by pressing the freshly pasted plates between polystyrene sheets at pressures of 700, 2000, and 5000 pounds. Those pressed at 700 pounds did not adhere well and were discarded. The advantage of the pressed electrode over the pasted lies in its flatter surface, diminished thickness, smaller volume, and absence of loose particles. A very compact plate was formed by applying five grams

of molten silver chloride directly to a silver grid. The approximate thickness of the various electrodes are given in Table 2.

TABLE 2

Pasted	0.070 "
Pressed at 2000 pounds	0.055 "
Pressed at 5000 pounds	0.047 "
Molten	0.038 "

No difficulty was experienced in anodically oxidizing the positive plates. A current of 0.25 ampere per plate was used in a 15% potassium hydroxide solution for 24 hours. These conditions are not critical, and the potassium hydroxide concentration can be varied widely with satisfactory results.

Both Merck's and Baker's silver chloride were used in preparing the positive plates. A screen test revealed a considerable difference in the particle size distribution between the two brands, but experimental evidence showed that the cell capacity was not affected thereby. Statistical analysis of forty cell discharges at different conditions using pasted, pressed, and molten positives showed no difference in cell capacities when sufficient silver oxide was present.

By increasing the electrolyte volume, or by decreasing the amount of silver peroxide present and using two negatives, the positive can be made to fail first. Such failures are due to an insufficient amount of silver oxides, even though all the silver oxides present are not completely utilized. A certain percentage of the silver oxides, approximately constant for a given set of conditions, is not available for cell reaction. The efficiency of utilization of silver peroxide for a given set of discharge conditions is the percentage of silver peroxide present that can be utilized by the cell. Its value can be determined by dividing the ampere minutes obtained from a particular discharge by the theoretical ampere minutes calculated from the weight of silver peroxide present. Table 3 gives the approximate efficiencies for different types of plates prepared by the methods described previously.

TABLE 3
Efficiency of Utilization of Silver Peroxide in Positive
Plates at 20° C. Using 40% KOH

	0.470 amp./in ²	0.235 amp./in ²	0.117 amp./in ²
Pasted	80.0	89.0	
Pressed at 5000 pounds	74.8	88.7	
Molten	68.9	88.2	89.1

Table 3 shows that, as the current increases above 0.235 ampere per square inch, the efficiency drops off the least on the most loosely packed electrode, which also occupies the most volume (the pasted), and drops off the fastest on the most closely packed, which occupies the least volume (the molten). This fact may be explained on the basis of availability of electrolyte to each silver peroxide particle.

These observations were made on thicker electrodes than would generally be used in actual cell construction. Theoretical considerations indicate that a thinner electrode will have a slightly higher efficiency. In the final design of a cell, any unnecessary excess of silver oxide would be cut to a minimum. Although the variation of the efficiency of utilization with current density and plate thickness must be considered in designing a cell of minimum weight or volume, it is not a factor of major importance in the majority of cases.**

Variation of Electrode Height

When zinc sheet is used as the negative electrode, the zinc does not dissolve evenly from the electrode face.** The rate of solution is several times as rapid at the top of the electrode as it is at the bottom.⁴ This difference is due partly to the concentration of the heavier zinc compounds in the electrolyte contained in the lower part of the cell. The variation of zinc dissolution with height necessitates the use of a considerable excess of zinc and may cause the cell capacity to vary with the electrode height.

When the electrode heights are varied from 0.75 to 4.5 inches, there is no significant variation in cell capacity as long as the electrolyte volume remains below 2 cc for each square inch of negative electrode area. However, at electrode heights above 2 inches, there is considerable decrease in capacity when this volume is exceeded. It is very improbable that any cell design will require that large an electrolyte volume. Therefore, the effect of electrode height on cell capacity may be safely neglected except where the length of the plate would affect its resistance.

Effect of Electrolyte Volume on Cell Capacity

If a sufficient volume of electrolyte is available, the capacities of many different cells are limited only by the amount of active materials present in the electrodes. Therefore, in designing a cell of minimum weight or volume, the effects of electrode spacing and electrolyte volume are of the utmost importance. However, in commercial batteries, study of the effects resulting from variation of these two factors has often been neglected since there are generally other requirements more important than minimization of cell weight or volume. This neglect has sometimes led to the belief that cell capacity per unit electrode area is of prime importance even though cell capacity per unit weight is often a more important factor. Unfortunately, many technicians have used excessive electrolyte volumes in laboratory experiments and as a consequence have obtained misleading results indicative of high cell capacities.

The effect of electrode spacing on the silver oxide cell capacity was studied, using sheet-zinc negative electrodes. Cell capacities were measured for electrodes spaced from 0.060 inch to 0.146 inch apart. Upon plotting the data for various concentrations of electrolyte and current density, smooth curves were obtained, apparently indicating a definite relationship. But upon further investigation, this proved to be a spurious correlation. The effects observed were found to be due to change in volume of electrolyte with change of electrode spacing. The electrode spacing itself, however, actually has a negligible effect on cell capacity.

A large number of measurements were made, using from 0.8 cc to 4.5 cc of potassium hydroxide solution per square inch of electrode area. Considerable difficulty was encountered for electrolyte volumes less than 1.6 cc per square inch because of the close electrode

**This problem will be discussed in a future NRL report.

spacing (0.015 inch to 0.030 inch). Polystyrene strips arranged in a star-like formation were used as spacers since the use of a continuous separator, such as a sheet of paper or cloth, would have introduced a new factor which might have reduced the cell capacity materially.

When these data were plotted, the relationship between cell capacity and electrolyte volume immediately became evident. As shown in Figure 2, a typical example, the data is fitted very well by a straight line running through the origin. Because of the importance of this relationship, exceptional care was taken to prove that it is general in nature. Extensive measurements were made at fourteen sets of conditions, in which the temperature varied from -20° to 40°C , the electrolyte concentration varied from 15% to 42.5%, and the current density varied from 0.0470 to 0.705 ampere per square inch. In every case, the relationships are very well fitted by a straight line of positive slope running through the origin and extending to a value which is dependent on the current density. Above a certain electrolyte volume, the observed data drops slightly below the straight line, as may be seen in Figure 3. The slopes of these lines are a function of the temperature, current density, and electrolyte concentration.

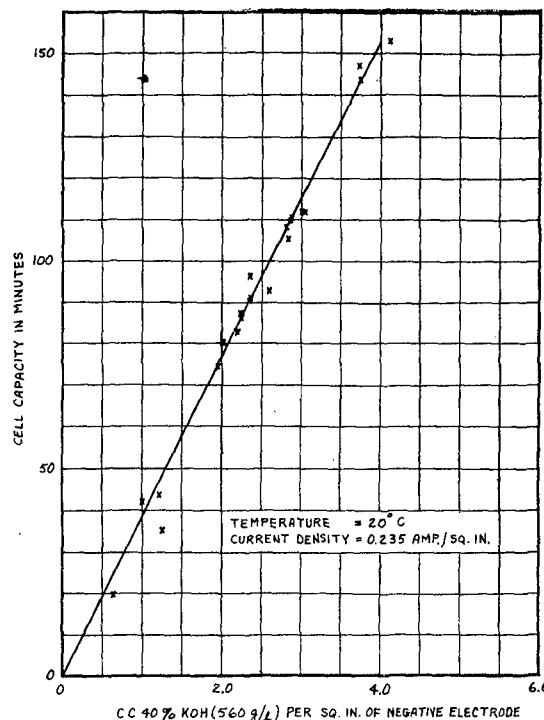


Figure 2 - Variation of cell capacity with electrolyte volume

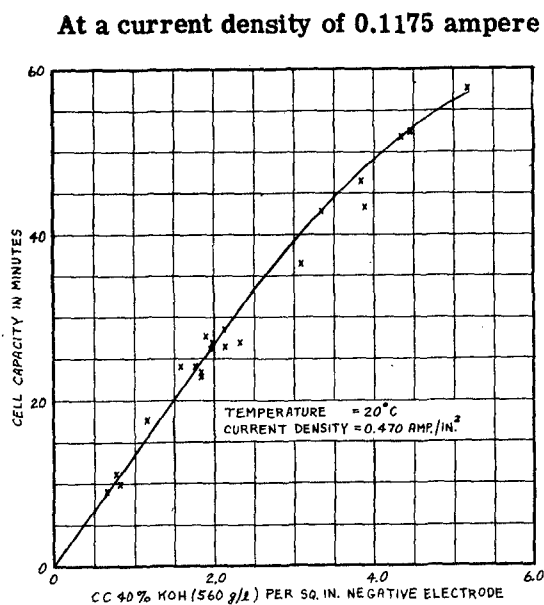


Figure 3 - Variation of cell capacity with electrolyte volume

At a current density of 0.1175 ampere per square inch, the linear relationship will hold for an electrolyte volume less than 3.5 cc per square inch of electrode area. As the current density increases to 0.470 ampere per square inch, the maximum electrolyte volume at which the linear relationship will hold decreases to about 3 cc per square inch of electrode area. These values are slightly lower for electrode heights of more than one and one-half inches. Since these limiting values of electrolyte volume are considerably larger than any that may generally be encountered in an ordinary cell, it is safe to use the straight-line relationship in cell design.

If the current density is increased sufficiently, a point is reached where the electrolyte composition in the surface films at the electrodes changes so rapidly that the cell fails before the surface film has a chance to diffuse into the rest of the electrolyte. At figures above the small volume involved in the surface films, the cell capacity is then

independent of volume. The current density at which this takes place has not been determined, but it is more than 0.705 ampere per square inch, which is a higher current density than is required in most cell designs.

When this linear relationship is examined, it is seen that the cell capacity is directly proportional to the volume, and a general formula for the relationship can be written in the form

$$C = kV, \quad (9)$$

where C is the capacity in minutes; V is the electrolyte volume per square inch of electrode area; and k is a constant depending on temperature, current density, and electrolyte concentration. Much of the data obtained has been for an electrolyte volume of 10 cc per unit cell, which value is equivalent to 2.35 cc of electrolyte per square inch of electrode area. If the capacity in minutes at 10 cc is equal to C_s , then

$$k = \frac{C_s}{2.35}, \quad (10)$$

and the formula becomes

$$C = \frac{C_s}{2.35} V. \quad (11)$$

Solving for C_s , we obtain

$$C_s = 2.35 \frac{C}{V}. \quad (12)$$

Equation 12 is very helpful in analyzing data. Some of the data used in determining this relationship was obtained under conditions such that a high percentage of electrolyte was not between the electrodes, but was behind or to one side of them. Although the results are not affected by this change, every effort was made in all cell constructions to keep most of the electrolyte between the faces of the electrodes. Therefore, it was impossible to use the same amount of electrolyte in every case. By using equation 12, it is possible to convert the capacity in minutes obtained with any electrolyte volume to the capacity that would have been obtained with a different volume.

The theoretical reason for the existing relationship between electrolyte volume and capacity is comparatively simple. Assume a cell operating on 1 cc of electrolyte, containing k_a milli-equivalents of potassium hydroxide, and failing after k_z milli-equivalents of zinc have been dissolved from the negative electrode. If, in forming some compound of zinc and potassium hydroxide, k_f equivalents of potassium hydroxide are consumed for each equivalent of zinc, then the composition of the electrolyte plus precipitate at the end of the discharge is

$$k_a - k_f \cdot k_z$$

milli-equivalents of potassium hydroxide per cc and k_z milli-equivalents of zinc compound per cc.

Under the same conditions, the relationship in equation 9 shows that if n cc of electrolyte are used, the cell capacity in minutes will be n times as long as the capacity obtained when 1 cc is used. Therefore, $n \cdot k_z$ milli-equivalents of zinc will be dissolved. At the end of the discharge, the electrolyte and precipitate will contain $n \cdot k_a - n \cdot k_f \cdot k_z$ milli-equivalents of potassium hydroxide and $n \cdot k_z$ of zinc—a composition which is the same

as that obtained when 1 cc of electrolyte was used. For a given set of conditions, the cell fails when the electrolyte reaches a certain composition, provided the electrolyte and precipitate are in equilibrium. Although these deductions are based on data obtained by using a zinc sheet electrode in a cell containing an excess of silver oxide and zinc, preliminary experiments indicate that the conclusions are also true when electroplated zinc electrodes are used.

An analysis of the data shows that there is sufficient information available to bring the battery under statistical control. A brief summary of the pertinent facts will verify this conclusion. The physical structure, method of preparation and method of anodizing the silver oxide electrode may vary over wide limits without affecting cell capacity as long as there is a sufficient amount of contaminant-free active material present.

The negative electrode is the one which fails first during cell discharge. Variation in its properties may cause a large variation in cell capacity. High-purity sheet zinc was selected as a standard because it simplified the measurement of current density. Each batch of sheet zinc was tested, and any that showed variation in results was rejected. The effect of variation in electrolyte volume on cell capacity from one run to another can be eliminated by arithmetical calculation. Variation in electrode height and spacing and minor changes in cell assembly have no effect on cell capacity. With all these factors under control, the effect of the remaining factors (temperature, current density, and electrolyte concentration) may be evaluated accurately.

Electrolyte Concentration

The variation of cell capacity with electrolyte concentration is shown in Figures 4 through 13 for a wide range of temperatures and current densities. The electrolyte volume is held constant at 2.35 cc per square inch of electrode area. The curves are characterized by a sharp increase in cell capacity with increase in electrolyte concentration, followed by an equally sharp decline. The cause of this break has not been determined, but it is probably due to a sharp decrease in solubility of the zinc compounds in the electrolyte.

Another interesting phenomenon was observed at low temperatures and low current densities. Very large variations in cell capacity are obtained for repeated runs at a particular set of conditions. On the basis of present information, it is not possible to predict at the beginning of a discharge whether a high, low, or intermediate cell capacity will be obtained. There are, however, high and low limits between which the capacity will fall. These have been plotted in Figures 10 and 12. The solid lines represent the lower limits, while the dotted lines represent the upper limits. In designing a cell at the present time, the lower curve must be used to be sure of obtaining a given cell capacity even though it is highly probable that a much greater capacity will actually be obtained. The data for the lower limits are used for further developments in this report.

Many of the discharges which give lower capacities are characterized by a sharp break in the discharge curve similar to that obtained with an internal short. However, if a break does not occur, a very high capacity is generally attained. At the end of a discharge, the space between the electrodes is completely filled with a very viscous white paste. The reaction occurring under these conditions appears to be entirely different from the reaction occurring at higher temperatures or current densities.

Observations of the entire series of curves in Figures 4 through 13 show that the variation of cell capacity with electrolyte concentrations, from the limit of about 250 grams per liter of potassium hydroxide up to the peak of the curve, may be fitted very well by a straight line passing through the origin. Since this is the region in which a properly designed cell would operate, this relationship may be considered a general one for the purpose of cell design.

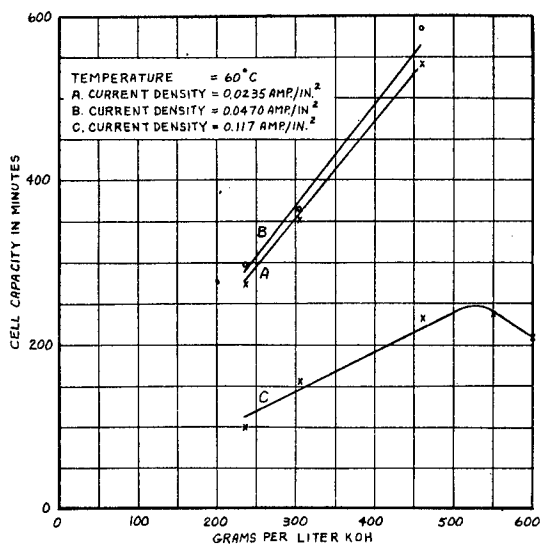


Figure 4

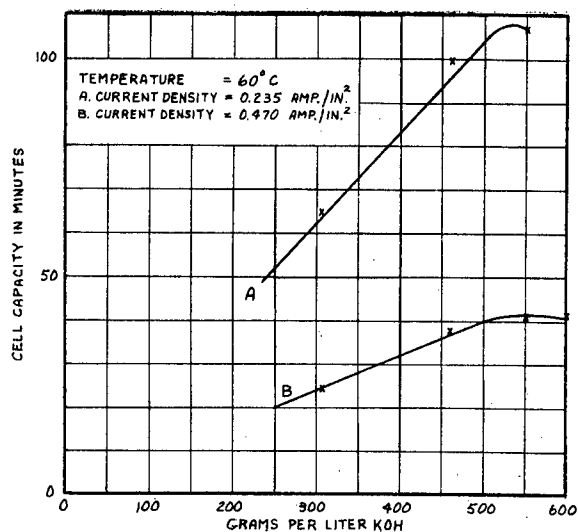


Figure 5

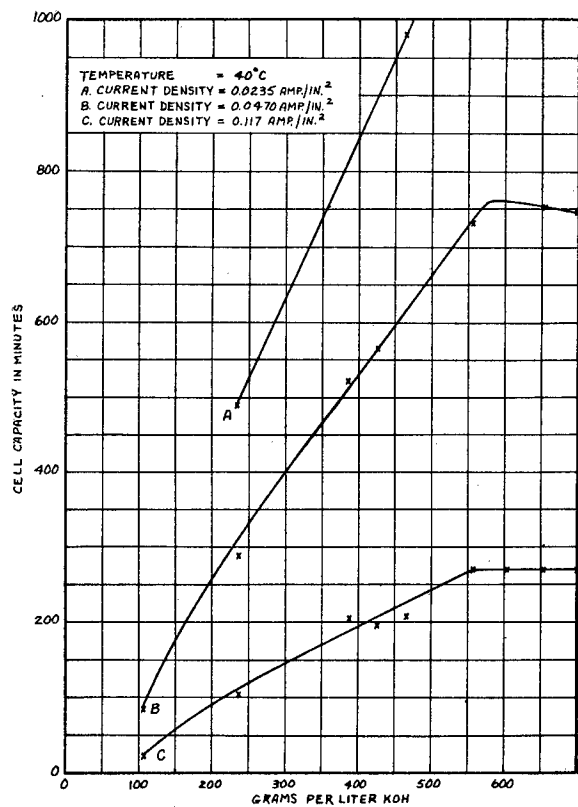


Figure 6

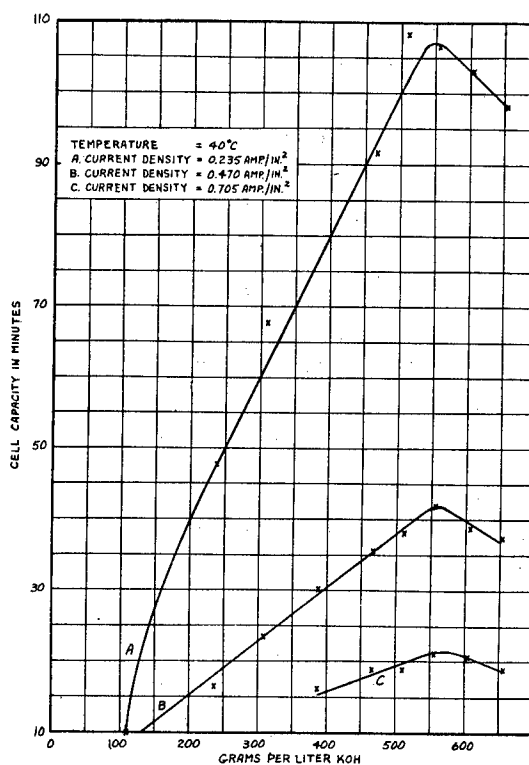


Figure 7

Variation of cell capacity with electrolyte concentration

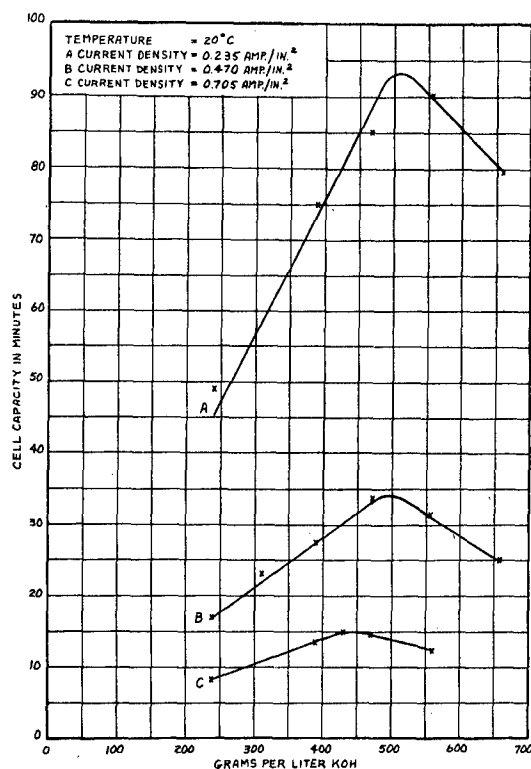
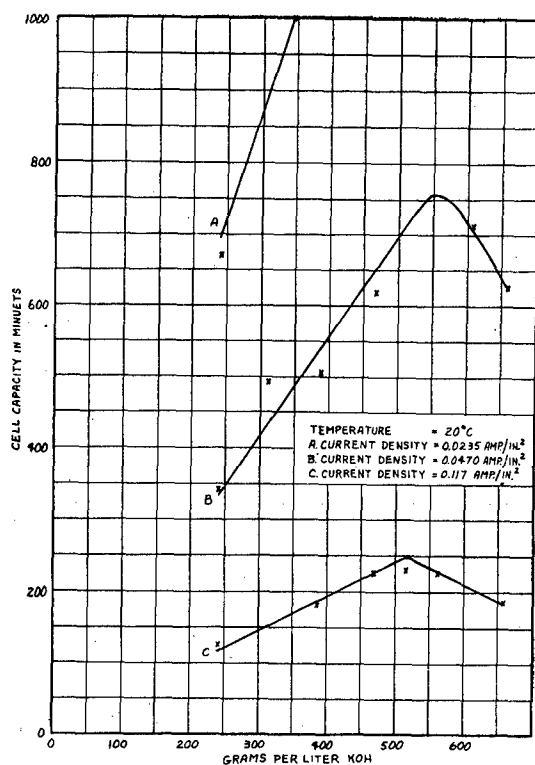


Figure 8

Figure 9

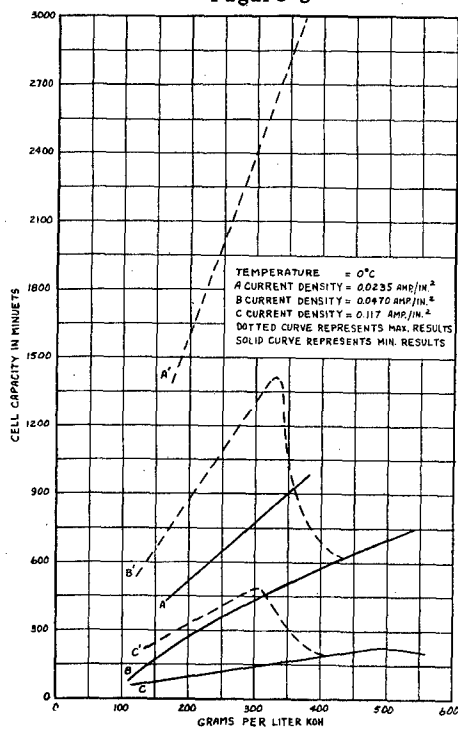


Figure 10

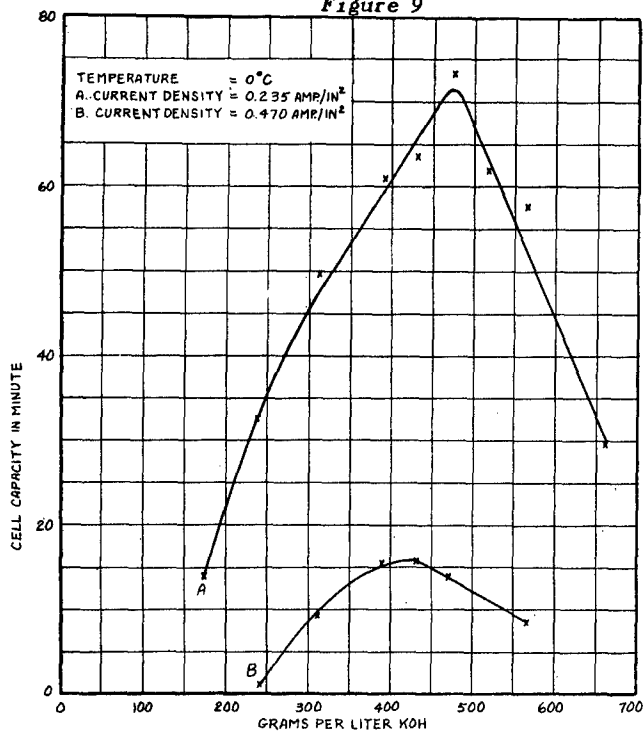


Figure 11

Variation of cell capacity with electrolyte concentration

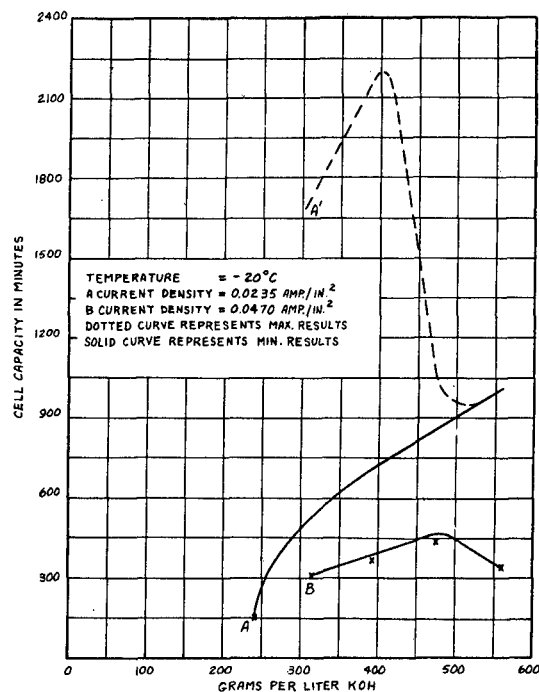


Figure 12

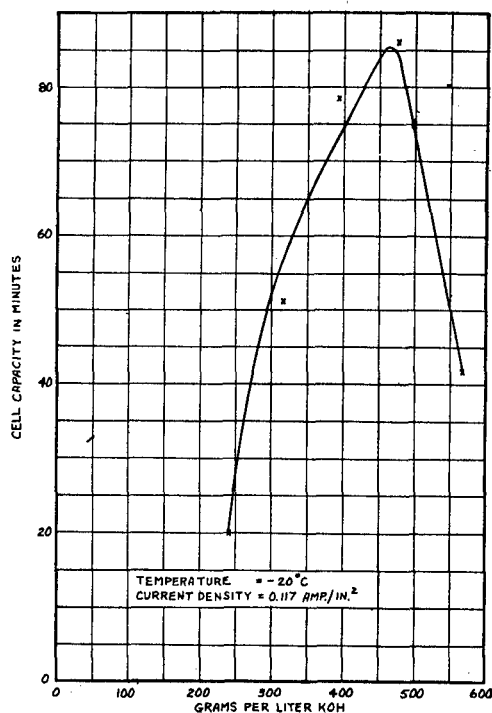


Figure 13

Variation of cell capacity with electrolyte concentration

Further examination of this relationship shows that the cell capacity is directly proportional to the electrolyte concentration, and a general formula can be written in the form

$$C = K_1 E, \quad (13)$$

where C is capacity, E is electrolyte concentration, and K_1 is a constant at any particular temperature, current density, and electrolyte volume. The relationship between cell capacity and electrolyte volume is

$$C = kV.$$

These two equations combine to give

$$C = K_2 VE. \quad (14)$$

However, the volume of the electrolyte times its concentration is equal to the amount of potassium hydroxide present in the solution. The equation for cell capacity then becomes

$$C = KW, \quad (15)$$

where K is a function of the temperature and current density, and W is the weight of potassium hydroxide present in the electrolyte. Within the limits of electrolyte volume and concentration previously mentioned, the cell capacity is directly proportional to the grams of potassium hydroxide used per unit electrode area. This relationship is illustrated in Figure 14.

Capacity

The cell capacity is directly proportional to the amount of zinc dissolved during discharge. Therefore the amount of zinc consumed is proportional to the amount of potassium hydroxide used, within the previously mentioned limits. An analysis of the electrolyte, plus any compounds precipitated by the end of a discharge, would show, at a given temperature and current density and for a wide range of electrolyte volume and concentration, a constant ratio of zinc consumed to the total amount of potassium present. This fact might lead one to believe that a particular compound of zinc and potassium was being formed. But such an implication is not warranted since the ratio of zinc and potassium varies greatly with change in current density and temperature.

The quantity K (shown in equation 15) is a function of current density and temperature and is plotted in Figure 15. The value, K, expressed as cell capacity per gram of potassium hydroxide per square inch of negative electrode area, has been plotted against current density at five different temperatures. Figure 15 shows the variation of cell voltage and cell capacity with temperature, current density, volume of electrolyte, and electrolyte concentration. Any calculation involving these variables is greatly simplified by use of this graph. The curve for 60°C, at the extreme left of the chart, shows a value of K equal to 240 minutes for a current density of 0.1 ampere per square inch. A cell having one square inch of negative electrode area and containing one gram of potassium hydroxide in the electrolyte would have a capacity of 240 minutes at this temperature and current density.

Use of this chart can further be illustrated by answering the question, "What is the capacity of a cell to be discharged at one ampere at 60°C if it has four negative electrodes 1 x 1-1/4 inches and contains 18 cc of KOH solution whose concentration is 500 g/l?"

The total area of both sides of the electrodes = $2 \times 4 \times 1 \times 1\frac{1}{4} = 10$ square inches.

The current density = $1 \text{ amp}/10 \text{ sq. in.} = 0.1 \text{ amp/sq in.}$, which corresponds to a value of 240 for K as read on the curve in Figure 15.

The amount of KOH in the cell is $500 \text{ g/l} \times 18 \text{ cc} = 9.0 \text{ grams}$.

The amount of KOH per unit area is $9.0 \text{ g}/10 \text{ sq. in.} = 0.9 \text{ g/sq. in.}$ The cell capacity in minutes equals K times the grams of potassium hydroxide per square inch of electrode area = $240 \times 0.9 = 216$ minutes. Hence, the cell will deliver a steady current of one ampere for 216 minutes at 60°C.

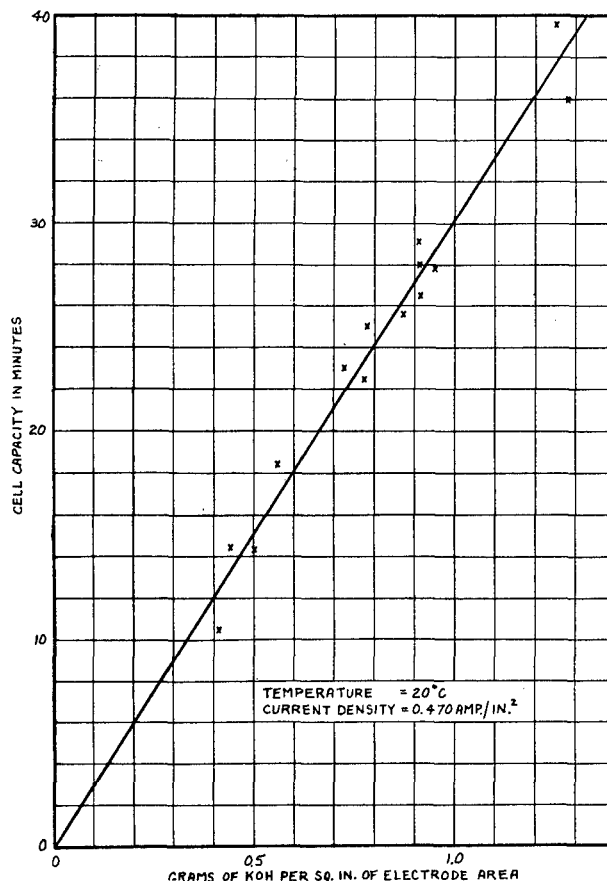


Figure 14 - Variation of cell capacity with weight of KOH.

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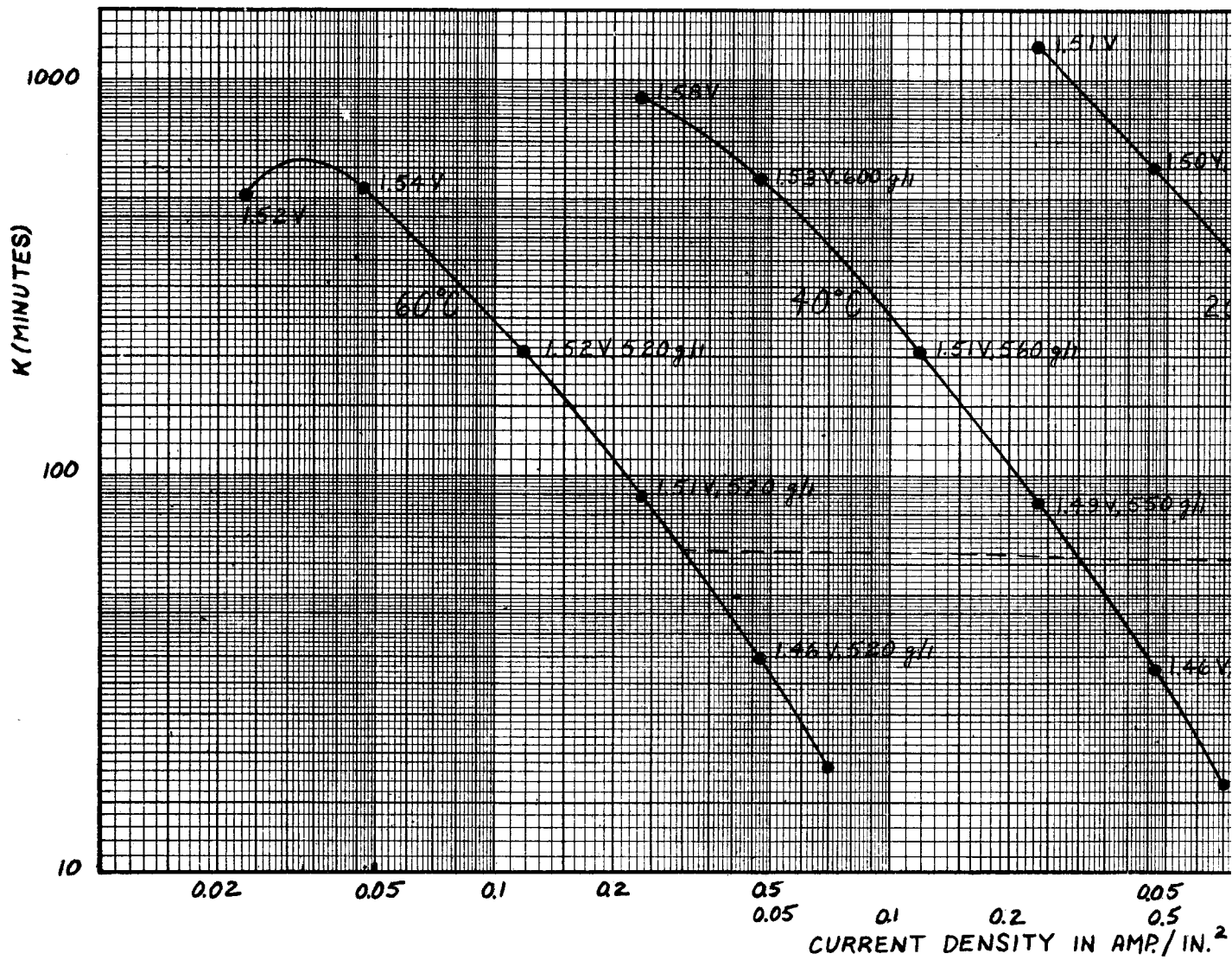
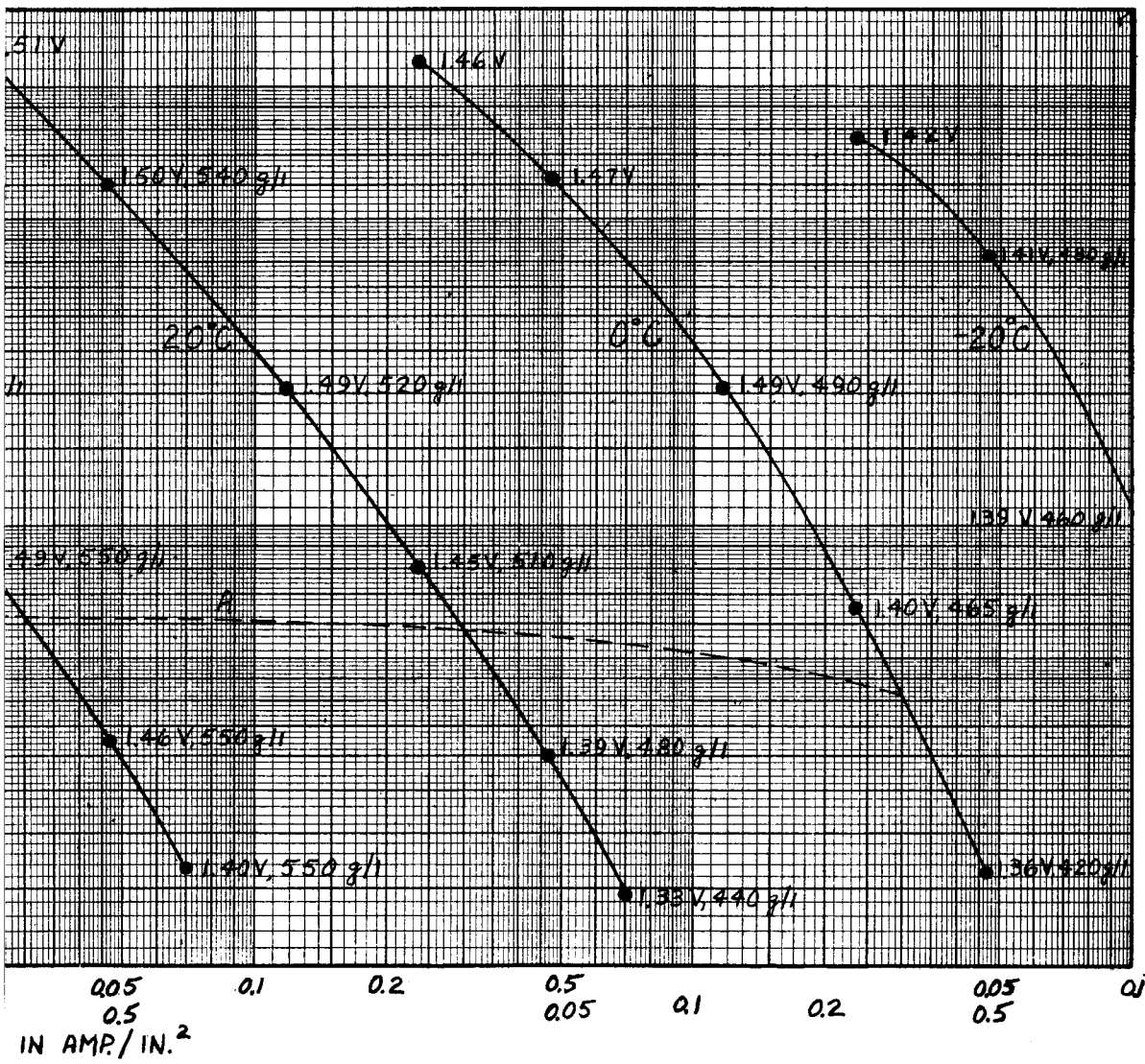


Figure 15 - Effect of variation in current density and temperature on cell capacity per gr.
(Including average voltage and optimum electrolyte concentration)

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capacity per gram of KOH per square inch of negative electrode area
(electrolyte concentrations)

At intervals along each curve in Figure 15 there is recorded the average voltage which can be obtained at that particular point and the maximum electrolyte concentration at which the linear relationship of equation 9 holds. These values of emf and electrolyte concentration are easy to interpolate since they do not vary rapidly. The current density of 0.1 ampere per square inch for the above cell falls on the curve near a recorded emf of 1.52 volts and an electrolyte concentration of 520 grams per liter. This value is the optimum concentration of electrolyte that can be used. It gives a cell capacity equal to $216 \text{ minutes} \times 520/500 = 225 \text{ minutes}$.

In Figure 15, the 40°C curve, which is found immediately to the right of the 60°C curve, is plotted against K in the same manner as the 60°C curve with the single exception that the current density coordinates have been shifted to the right. The point on the abscissae which corresponds to 0.5 ampere per square inch for the 60°C curve corresponds to 0.05 ampere per square inch for the 40°C curve. A similar and equal shift of the current density coordinates is made on each of the successive temperature curves across the chart. The temperature difference between each successive curve is constant, and the distance between any particular current density (such as 0.1 ampere per square inch) is constant for each successive curve.

Thus, it is possible to draw a new curve that shows the variation of K with temperature at any particular current density. For example, curve A gives values of K at different temperatures for a current density of 0.3 ampere per square inch. The abscissa of A, which is graduated linearly, is temperature. The 60°C point on the abscissa of A is at the point corresponding to 0.3 ampere per square inch on the 60°C curve, and the 0°C location is at the point corresponding to 0.3 ampere per square inch on the 0°C curve. By interpolation, the values of K at any temperature can readily be obtained. For instance, the value of K for 10°C lies halfway between the 0°C curve and the 20°C curve and is equal to 52 minutes.

A mathematical analysis of the curves in Figure 15 shows that the major portion of them can be fit by the empirical equation,

$$\log K = a + b \log I + c(\log I)^2, \quad (16)$$

where I is the current density in amperes per square inch and a, b, and c are parameters which vary with temperature. Values of a, b, and c, listed in Table 4, are plotted against temperature in Figure 16. The value of K can be predicted accurately from the parameters for current densities between 0.470 and 0.0470 ampere per square inch at temperatures between 0°C and 60°C; and for temperatures between -5°C and -20°C, K can be predicted for current densities between 0.235 and 0.0235 ampere per square inch. Cell characteristics can be calculated readily with this information whenever the data falls within the limitations imposed on the current density and electrolyte volume and concentration. Almost all cell designs are in this area.

Considerable care must be taken in obtaining parameter values from Figure 16, since a slight error in the sharply sloping region of the curves may cause a considerable error in the predicted value of K. More accurate results may be obtained with data taken from the horizontal portions of the curves. In general, values of K derived from Figure 16 are not as accurate as those obtained from Figure 15 by interpolation or from Table 4 by calculation. Suppose the characteristics are desired for a battery, to be discharged at

TABLE 4

Temperature	a	b	c
60°C	1.0412	-1.5971	-0.2575
55	1.0314	-1.590	-0.240
50	1.0268	-1.585	-0.225
45	1.0134	-1.59	-0.215
40	1.0016	-1.602	-0.210
35	0.9864	-1.620	-0.211
30	0.9688	-1.644	-0.216
25	0.9494	-1.667	-0.223
20	0.9242	-1.707	-0.238
15	0.8794	-1.780	-0.262
10	0.7949	-1.917	-0.315
5	0.6554	-2.170	-0.427
0	0.4194	-2.61	-0.615
-5	0.0394	-3.13	-0.805
-10	-0.3906	-3.70	-1.00
-15	-0.9106	-4.31	-1.19
-20	-1.5325	-4.959	-1.38

11.75 amperes and 40°C, which has 100 square inches of electrode area and contains 235 cc of KOH solution at a concentration of 400 grams per liter. Values of a, b, and c at 40°C taken from Table 4 are 1.0016, -1.602 and -0.210, respectively. Substituting in equation 16,

$$\log K = 1.0016 - 1.602 \log 11.75/100 - 0.210 (\log 11.75/100)^2,$$

and K = 204 minutes, which value could have been obtained directly from Figure 15.

The grams of potassium hydroxide present per wquare inch of electrode area equals

$$235/100 \times 400/1000 = 0.94.$$

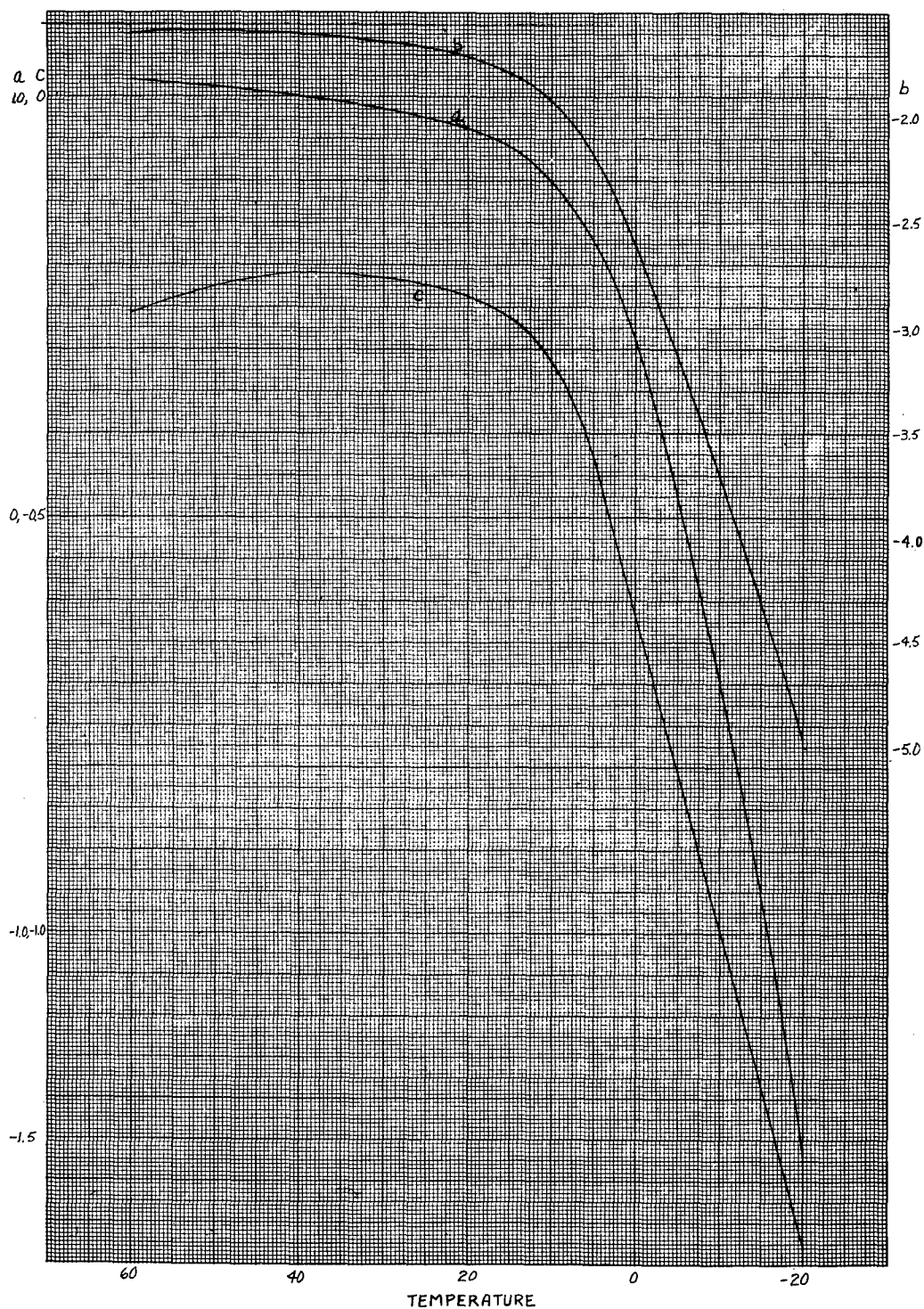


Figure 16 - Parameters a , b , c , for the equation for calculating cell capacity

The capacity of the cell equals 204, the values of K, times 0.94 or 192 minutes, which corresponds to the value given in curve C, Figure 6. The emf of the cell is found from Figure 15 to be 1.51 volts. The most effective concentration of electrolyte that can be used is 560 grams KOH per liter, which gives a cell capacity, under these conditions, equal to $192 \times 560/400$ or 267 minutes.

Voltage Characteristics

A typical discharge curve using newly prepared silver electrodes is shown in curve 1, Figure 17. As soon as the load is applied, the voltage drops very rapidly to a value which stays fairly constant until the discharge is nearly completed. During the main body of the discharge, the voltage drops less than 0.10 volt.

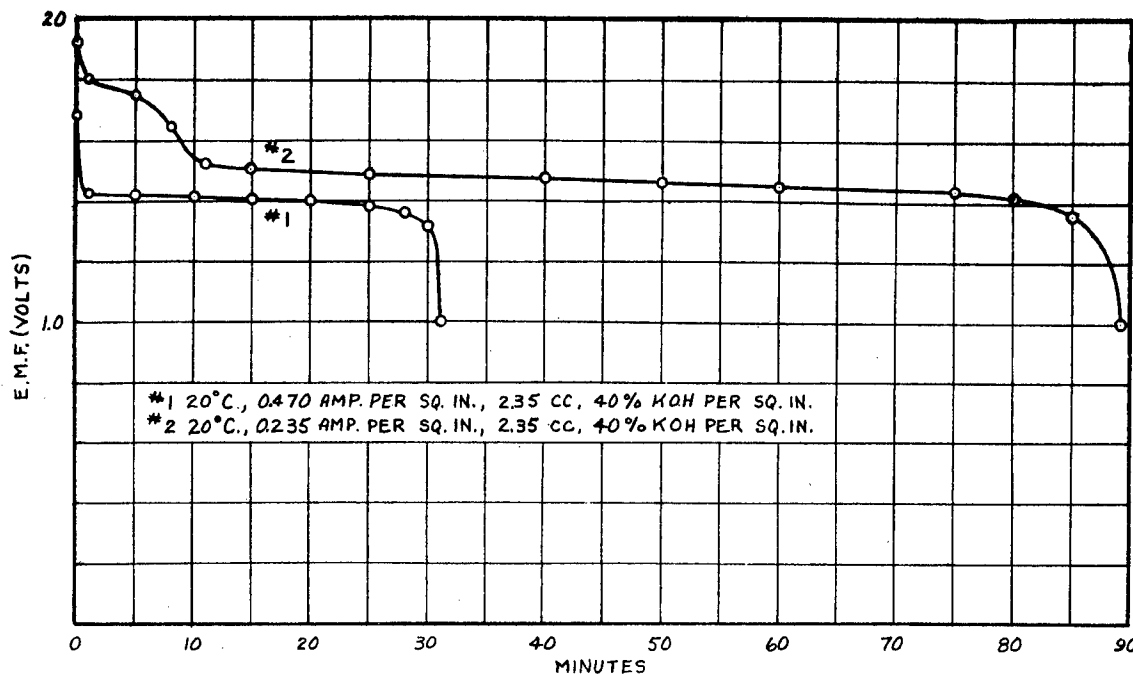


Figure 17 - Typical discharge curves

Although the positive electrodes can be charged and reused a number of times without affecting the cell capacity, the recharging does affect the voltage characteristics. A typical curve using recharged positives is shown in curve 2, Figure 17. When the load is applied in this case, the emf drops down slowly for a varying length of time until it reaches its regular constant value. This higher initial voltage, over a varying period of time, is probably caused by the presence of a higher oxide of silver which is slowly formed during the recharging.

High Current Densities

Many of the potential demands for the silver oxide cell are based on the fact that it is capable of delivering current at a very high current density. Some of these requirements can be fulfilled by conditions which have already been evaluated. Other demands may involve current densities so high that they can be obtained only by using negative electrodes of large surface area, such as pasted or electroplated negatives.

A few exploratory measurements were made using sheet-zinc negatives at a current density of 1.175 amperes per square inch and an electrolyte volume of 2.35 cc per square inch. The results, plotted in Figure 18, have a very high coefficient of variation and are subject to considerable error. No attempt was made to determine the effect of electrolyte volume. It is probable, however, that the same capacity could have been obtained with only a fraction of the electrolyte actually used.

Low-Temperature Characteristics

There has been some research done on special cells which can be used at low temperatures only. The silver oxide cell shows considerable promise of fulfilling the present demand for a cell which will operate at normal temperatures as well as low temperatures. The high current densities, its outstanding feature at ordinary temperatures, cannot be used at low temperatures. However, very large capacities can be obtained by using low current densities, under which conditions the power output per unit weight of cell is quite high but is still much less than would be obtained at higher temperatures.† Results of a few preliminary discharges made at -40°C are plotted in Figures 19 and 20. The data in Table 5 was also obtained using 30% (396 g/l) KOH.

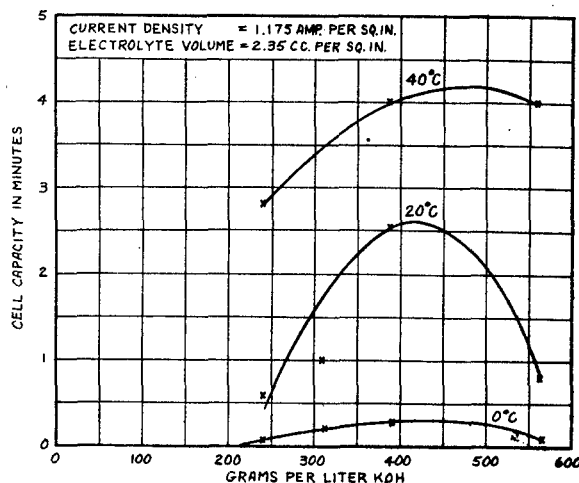


Figure 18 - Variation of cell capacity with temperature and electrolyte concentration at high current density

TABLE 5

Temperature	Current Density amp./in. ²	Cell Capacity in Min.	E.M.F.
-44°C	0.0235	39.4	1.39
-50°C	0.01175	148	1.43
-52°C	0.00588	665	1.45

At -50°C potassium hydroxide is liquid between the concentrations of 360 and 490 grams per liter, and at -60°C it is liquid between 390 and 460 grams per liter. Almost every electrolyte used in ordinary cells is solid at these temperatures or else is liquid over a very narrow range. Should the composition or concentration of the electrolyte change, as is usually the case during discharge, then it may fall outside the liquid range and freeze, thus rendering the cell incapacitated. It is not necessary that the entire body of the electrolyte be frozen. The film next to the electrode, or that portion of the electrolyte held in the pores of a porous electrode, will be subject to the most change in composition. If either of these portions freezes, the cell will be incapacitated.

† Cells using zinc-plated wire screen negative electrodes have a higher capacity because their large surface area results in a lower actual current density. This will be discussed in a future NRL report.

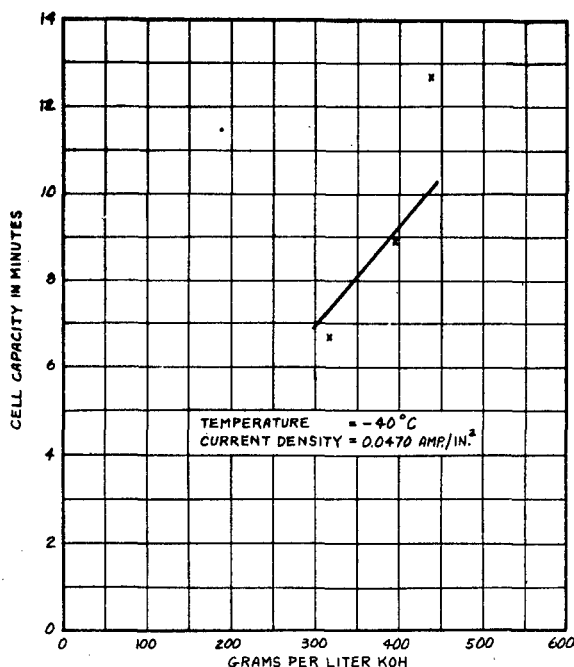


Figure 19 - Variation of capacity with electrolyte concentration

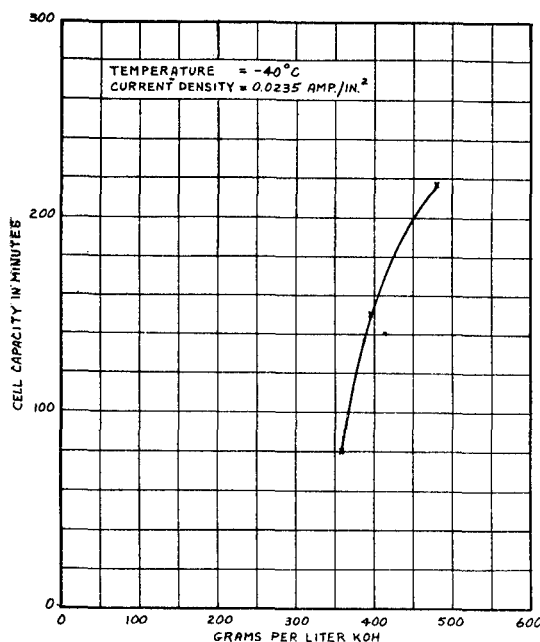


Figure 20 - Variation of cell capacity with electrolyte concentration

Since the cell capacity is so very much greater at higher temperatures, any factor which will raise the temperature of the cell will also improve its capacity. A number of experiments were made wherein a small amount of concentrated acid was added to the cell along with the potassium hydroxide solution. The heat of reaction raised the cell temperature thereby improving the cell capacity. Some results are given in Table 6 for runs made at -25°C and 0.235 ampere per square inch current density using 35% (476 grams per liter) potassium hydroxide. A standard run at this temperature using 10 cc of 35% potassium hydroxide per cell gave a capacity of five minutes. Since the acid neutralized a portion of the potassium hydroxide, no quantitative comparison can be made, but it is possible that the capacity can be increased at least 100% in this particular case. However, this method would work only on short discharges since the cell would eventually cool down again if operated in cold surroundings.

TABLE 6

Cell Capacity in Minutes	Cc Electrolyte per Cell	Cc of Acid per Cell
4.9	8	2 cc 80% H_2SO_4
8.1	10	1 cc 80% H_2SO_4
6.6	10	1 cc conc. HCl
9.75	10	1 cc HI
10.1	10	1 cc conc. HNO_3

If a sufficient amount of electrical energy is needed at a low temperature, it would be practical to design a battery case with a built-in heating unit. A small burner operating on a liquid fuel could furnish an effective lightweight source of heat. For a medium-sized battery, the saving in weight might be quite large. Such a construction would necessitate a considerable amount of design and testing but might prove extremely effective.

CONCLUSIONS

The capacity of a silver oxide-zinc alkaline cell using zinc-sheet negative electrodes has been found to be a function of the current density, temperature, electrolyte concentration and electrolyte volume. This function has been evaluated mathematically and graphically. Within limits, a decrease in current density, or an increase in electrolyte volume of electrolyte concentration, will cause an increase in the cell capacity.

The current density may be decreased, in cell design, by increasing the number of plates in the cell. However, this will result in an increase of grid weight which opposes any gain obtained by decreasing the current density. These two factors must be properly balanced in designing a cell of minimum weight. Similarly, any increase in cell capacity obtained by increasing electrolyte volume per unit area is opposed by an increase in weight of electrolyte or by a decrease in current density caused by the decrease in electrode area. A mathematical analysis of some type is necessary whenever an effective cell design is desired.

Preliminary work has shown that the use of negative electrodes having a large surface area will increase cell capacity appreciably at high current densities and at low temperatures.

RECOMMENDATIONS

On the basis of the information that is needed, and of that which is available, it is recommended that the following projects be given immediate attention:

- (a) Investigation of separators with the object of finding satisfactory materials and of evaluating their effect on cell characteristics;
- (b) Investigation of negative electrodes having a large surface area with the idea of developing a cell that will operate satisfactorily both at high current densities and at low temperatures;
- (c) Investigation of positive grid materials with the object of finding a satisfactory light-weight material;
- (d) Development of mathematical and graphical methods of presentation of data for ready utilization in designing the most effective cell possible for any given set of requirements;
- (e) Investigation of the theory of the cell.

* * *

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The silver oxide-zinc alkaline primary cell - Part 1 - Effect of temperature and of volume and concentration of electrolyte on the relationship between capacity and current density for a cell using sheet-zinc negative plates, by C. M. Shepherd. Washington, Naval Research Laboratory, July 1, 1949.

27 pp. illus. 27 cm.

Abstract: The outstanding properties of the silver oxide-zinc alkaline cell are its low weight, high current density, constant voltage, and high capacity at low temperatures. Experimental work, subjected to statistical control, showed that cell failure always occurs at the negative electrode if sufficient silver oxide is present at the positive plate. Presence of copper diminishes cell capacity. The physical structure of the silver electrode, and the method of preparation and anodizing, can all be varied over wide limits without affecting cell capacity. Variations in electrode height and spacing do not affect cell capacity.

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Naval research laboratory. Report no. C-3478.

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1. Batteries, primary. 2. Electrolytes. I. Shepherd, C. M. CONFIDENTIAL

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